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THE SYNTHESIS AND CHARACTERIZATION OF TELLURANTHRENE

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Summary

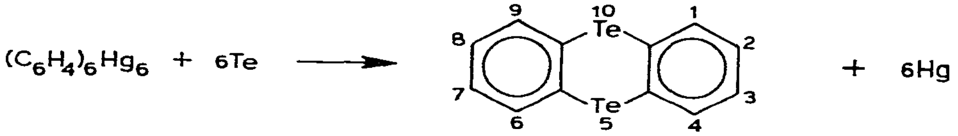
The reaction between *o*-phenylenemercury and finely powdered tellurium metal at temperatures not exceeding 250°C yields a pale yellow crystalline solid. Characterization of this solid by elemental analysis, determination of the molecular mass, mass spectral analysis, and ^{13}C and ^{125}Te NMR spectral analysis indicates that it is the hitherto uncharacterized telluranthrene.

Introduction

The preparation of telluranthrene by the reaction between tetraphenyltin and tellurium metal was reported in 1964 [1]. Telluranthrene was described as a brown, air-sensitive solid, melting at 188—190°C and depositing tellurium upon exposure to the atmosphere. Because of our interest in heterocyclic tellurium compounds we have, on a number of occasions, attempted without success, to duplicate this synthesis. A number of organometallic syntheses have been reported which depend upon the volatility of Me_2SnCl_2 e.g.,

$$R_2SnCl_2 + Me_2AsCl \rightarrow R_2AsCl + Me_2SnCl_2$$

It was decided, therefore, to attempt the preparation of telluranthrene by the reaction of $TeCl_4$ with *Sn,Sn*-tetramethylstannanthrene. The latter compound, however, is prepared from *o*-phenylenemercury. Hence, it seemed reasonable to investigate the reaction between elemental tellurium and the mercury compound. This type of reaction has been reported previously [2]. This reaction was found to yield telluranthrene and its preparation and characterization are the subject of this report.



Experimental

The melting point was determined using a Büchi-SMP-20 melting point apparatus (capillary method) and is uncorrected. The ^1H NMR spectrum was recorded on a Varian T-60 spectrometer and the ^{13}C NMR spectra were measured on a JEOL-PFT-100 using $CDCl_3$ as the solvent and TMS as an internal reference standard. The Te NMR of ^{125}Te was observed at 63.20 MHz on a Varian XL-200 spectrometer equipped with a synthesizer and Fourier transform equipment. Chemical shifts are reported in parts per million (δ) and in the case of ^{125}Te NMR are expressed relative to CH_3TeCH_3. The mass spectra were recorded on a Du Pont CE21-110B spectrometer operating at an ionizing potential of 70 eV. Microanalyses and molecular mass determination were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee.

Telluranthrene

o-Phenylenemercury [3] (2.5 g, 4.5 mmol) and finely powdered tellurium (2.3 g, 18 mmol) were intimately ground together and placed in the well of a sublimation apparatus. The pressure in the sublimation apparatus was reduced to one torr, or lower, and the well of the apparatus, containing the reaction mixture, was taken to 250° C and maintained for 10 h at this temperature in a bath of Wood's metal. During this time both elemental mercury and a crystalline material condense on the cold-finger (Dry Ice) of the sublimation apparatus. The sublimed solids are dissolved in chloroform and filtered to remove the mercury. Evaporation of the solvent leaves light yellow crystals subsequently identified as telluranthrene. The yield was 1.33 g (3.25 mmol) corresponding to 72%. Thin layer chromatography on silica gel PF_{254} (Merck) using carbon tetrachloride as the eluent gave a single spot, $R_f = 0.61$. Recrystallization from ethanol/benzene or carbon tetrachloride gave 1.05 g of pale yellow crystals melting at 169—170° C. Anal. found: C, 35.11; H, 1.96; Te, 62.39. $C_{12}H_8Te_2$ calcd.: C, 35.36; H, 1.96; Te, 62.67%. Molecular mass, found (vapor pressure osmometry, benzene): 421 ± 20, calcd.: 407.4.

Results and discussion

Mass spectral data

In this discussion, relative intensities will be referred to that of diphenylene ($M = 152$) taken as unity. The following molecular ion peaks (intensities) for telluranthrene were observed: 412 (0.45), 410 (0.83), 408 (0.95), 406 (0.66). The relative intensities are consistent with those expected for the statistical distribution in organic molecules bearing two tellurium isotopes [4]. Telluranthrene undergoes fragmentation by several routes. Loss of one tellurium results in formation of dibenzotellurophene, $C_{12}H_8Te^{\cdot+}$, 282 (0.94). The latter, in turn, by further loss of tellurium, fragments to diphenylene $C_{12}H_8^{\cdot+}$, 152 (1.00). Diphenylene can also form by the loss of two tellurium atoms from telluranthrene. Loss of C_6H_4 from telluranthrene yields *o*-phenyleneditelluride, $C_6H_4Te_2^{\cdot+}$, 336 (0.15) which, by loss of one tellurium yields a fragment of mass 206 (0.21), presumably, *o*-phenylenetelluride, $C_6H_4Te^{\cdot+}$, $Te_2^{\cdot+}$ and $Te^{\cdot+}$ fragments are easily identified in the mass spectrum. Other organic fragments which predominate are C_6H_4, C_6H_3, C_6H_2 and C_4H_2.

Nuclear magnetic resonance

The proton decoupled ^{13}C NMR spectrum is characterized by intense resonances at 128.3 and 136.5 ppm and a weak resonance at 130.6 ppm. Side bands due to ^{125}Te coupling are easily observed.

The resonance at 136.5 ppm is attributed to carbon atoms 1, 4, 6, and 9 and the coupling constant, $^2J(C(1)—Te)$ is 53.3 Hz. The 128.3 ppm resonance is assigned to carbon atoms 2, 3, 7, and 8 and $^3J(C(2)—Te)$ is 12.5 Hz. At 130.6 ppm the resonance is attributed to the carbon atoms directly bonded to tellurium and $^1J(C_\alpha—Te)$ is unusually large, 282.4 Hz. This may represent the first observation of a coupling constant between tellurium and an aromatic carbon. For comparison, in dimethyl telluride [5,6], $^1J(C—Te)$ has been reported to be 162 Hz while in dimethyltellurium dichloride, $(CH_3)_2TeCl_2$, $^1J(C—Te)$ has been found to be 175.3 Hz [7]. In the case of telluranthrene, the much higher value of the coupling constant can be attributed, at least in part, to the sp^2 character of the carbon located α to tellurium. The carbon in $H_3C—Te$ compounds is sp^3 hybridized. Inasmuch as the ^{13}C resonance in neat benzene is observed at 128.7 ppm the resonance at 128.3 ppm can be assigned to carbon atoms 2, 3, 7, and 8 with considerable confidence. The assignment can be further corroborated since it displays the smallest coupling constant to tellurium. The order in the values of the coupling constants is consistent with the number of atoms they are removed from one another. It is also to be noted that the values of the integrated peak intensities were in good agreement, within 1.5 per cent, of the values expected for the relative abundance of ^{125}Te, vis., 6.99 per cent.

The ^1H NMR spectrum of telluranthrene was characterized by a pair of aromatic multiplets at 7.9 and 7.1 ppm. The latter is attributed to protons attached to carbon atoms 2, 3, 7, and 8 as they are closer to the proton resonances observed in benzene.

Finally, the ^{125}Te NMR resonance was easily observed as a singlet at 888 ppm relative to dimethyltellurium. The two tellurium atoms are obviously equivalent.

Mechanistic possibilities

No studies have yet been undertaken to determine the mechanism of this reaction, but it seems very likely that a free radical mechanism is involved. The thermal decomposition of organomercury compounds via free radical mechanisms has been the subject of a large number of studies [8]. The crystal structure of *o*-phenylenemercury has been determined [9] and it has been found to be hexameric, $[Hg\text{-}o\text{-}C_6H_4—Hg\text{-}o\text{-}C_6H_4]_3$. The carbon—mercury bond can thermally dissociate into $—C_6H_4—Hg^\cdot + {}^\cdot C_6H_4—Hg—$. A free radical reaction with tellurium is easily envisioned, i.e.,

$$—Hg—C_6H_4^\cdot + Te \rightarrow —Hg—C_6H_4—Te^\cdot$$

This can be followed by a second radical dissociation and subsequent reactions with tellurium, e.g.,

$$—Hg—C_6H_4^\cdot + {}^\cdot Te—C_6H_4—Hg— \rightarrow —Hg—C_6H_4—Te—C_6H_4—Hg—$$

$$—Hg—C_6H_4—Te—C_6H_4—Hg— \rightarrow —Hg^\cdot + {}^\cdot C_6H_4—Te—C_6H_4—Hg—$$

$$^{\bullet}C_6H_4{-}Te{-}C_6H_4{-}Hg{-} + Te \rightarrow {}^{\bullet}Te{-}C_6H_4{-}Te{-}C_6H_4{-}Hg{-}$$

$$^{\bullet}Te{-}C_6H_4{-}Te{-}C_6H_4{-}Hg{-} \rightarrow {}^{\bullet}Te{-}C_6H_4{-}Te{-}C_6H_4{}^{\bullet} + {}^{\bullet}Hg{-}$$

$$^{\bullet}Te{-}C_6H_4{-}Te{-}C_6H_4{}^{\bullet} \rightarrow \text{telluranthrene}$$

The complete replacement of all mercury atoms by tellurium, i.e., formation of $[Te\text{-}o\text{-}C_6H_4{-}Te\text{-}o\text{-}C_6H_4]_3$ and its subsequent thermal rearrangement to telluranthrene is possible, but improbable.

The inability to successfully synthesize this compound heretofore is probably due to the use of temperatures that were too high. Thermally, the molecule will convert, by extrusion of tellurium, to dibenzotellurophene and to diphenylene. We have successfully reproduced this synthesis on at least four occasions without difficulty.

A data set is being collected on single crystals of this compound and its structure will be reported in the near future.

Selenanthrene

Selenium powder was substituted for tellurium and the reaction with *o*-phenylenemercury was repeated in the manner described for the preparation of telluranthrene. As the temperature of the heating bath was raised, a rather violent reaction occurred. Dissolution and filtration of the reaction mixture, followed by recrystallization afforded a small quantity of selenanthrene. The latter was identified by its melting point and mixed melting point with an authentic sample. Although the method works, the yield is very poor ($<5\%$) and previously published methods for the synthesis of selenanthrene are superior.

Acknowledgement

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